PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2004-331757
(43)Date of publication of application : 25.11.2004

(51)Int.Cl. C08L 67/04
// C08L101/16

(21)Application number : 2003-127779
(22)Date of filing : 06.05.2003

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(54) POLY(3-HYDROXYALKANOATE) COMPOSITION AND METHOD FOR PRODUCING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To improve formability such as fusion prevention, line speed improvement, etc., in the use of formation method such as melt extrusion molding, molten film formation, melt spinning, etc., by raising the melt strength of a polyhydroxyalkanoate melt having inferior melt strength in melt processing and improving crystallization rate.
SOLUTION: The poly(3-hydroxyalkanoate) composition (ab) is obtained by mixing a poly(3-hydroxyalkanoate) composition (a) having melt temperature Tma with a poly(3-hydroxyalkanoate) composition (b) having melt temperature Tmb (Tmb≥Tma+5° C). The composition (ab) has melt viscosity ηab at an arbitrary temperature Te (Tma≤Te≤Tb) with relation ηa<ηab to melt viscosity ηa at the Te of the composition (a).

LEGAL STATUS

[Date of request for examination] 28.03.2006
[Date of sending the examiner's decision of rejection]
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]
[Date of final disposal for application]
[Patent number]
[Date of registration]
[Number of appeal against examiner's decision of rejection]
[Date of requesting appeal against examiner's decision of rejection]
[Date of extinction of right]

CLAIMS

[Claim(s)]
[Claim 1]
It is the Pori (3-hydroxy alkanoate) constituent shown by the formula (1).
Constituent (a): The Pori (3-hydroxy alkanoate) constituent which has weight average molecular weight Mwa (1x104 <=Mwa<=3x106) and a melting out temperature Tma.
Constituent (b): The Pori (3-hydroxy alkanoate) constituent which has weight average molecular weight Mwb (1x104 <=Mwb<=1x107) and a melting out temperature Tmb (here, it is Tmb>=Tma+5 degree C).
It is the Pori (3-hydroxy alkanoate) constituent (ab) mixed and obtained.
The Pori (3-hydroxy alkanoate) constituent with which melt viscosity etaab in Te (however, Tma<=Te<=Tmb) of the arbitration of a constituent (ab) has the relation of eta a<eta ab to melt viscosity etaa in Te of a constituent (a) (ab).
[-CHR-CH2-CO-O-] ..... Formula (1)
Here, R is the alkyl group expressed with CnH2n+1, and is n=1-15.
[Claim 2]
The constituent according to claim 1 whose constituent (a) is Pori (3-hydroxy butyrate-KO-3-hydroxy hexanoate).
[Claim 3]
The constituent according to claim 2 whose constituent (a) the presentation ratio of the copolymerization component is Pori (3-hydroxy butyrate):Pori (3-hydroxy hexanoate) =99-80:1-20 (mol%) in Pori (3-hydroxy butyrate-KO-3-hydroxy hexanoate) and whose constituent (b) is Pori (3-hydroxy butyrate).
[Claim 4]
A constituent (a) and a constituent (b) are Pori (3-hydroxy butyrate-KO-3-hydroxy hexanoate). The presentation ratio of the copolymerization component of a constituent (a) by 3-hydroxy butyrate:3-hydroxy hexanoate =99-80:1-20 (mol%) And the constituent according to claim 2 with which the presentation ratio of the 3-hydroxy hexanoate component of a constituent (b) is characterized by being smaller than the presentation ratio of the 3-hydroxy hexanoate component of a constituent (a).
[Claim 5]
A constituent given in any 1 term of claims 1-4 whose mixing ratios of the constituent (a) in a constituent (ab) and a constituent (b) are (a):(b) =70:30-99.9:0.1.
[Claim 6]
The approach of carrying out heating fusion of a constituent (a) and the constituent (b), and mixing, the approach of mixing in a solvent using a meltable solvent, How to mix a constituent (b) in the slurry obtained in the purification phase after (Constituent a) culture, And the manufacture approach of a constituent (ab) given in any 1 term of at least one or more sorts of claims 1-5 chosen from the group which consists of the approach of changing a presentation during culture of a constituent (a), creating a constituent (b), and mixing.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]
This invention relates to the polyester system resin constituent which has biodegradability, and its manufacture approach. In more detail, it excels in aerotropism and the biodegradability under an anaerobic environment at the time of abandonment, and even if it carries out incineration processing, there is little calorific value, and the natural polyhydroxy alkanoate which the microorganism produced is used and it is related with the manufacture approach of a constituent that a melt viscosity property and a crystallization rate gentle to earth environment have been improved.
[0002]
[Description of the Prior Art]
Conventionally, plastics has been thrown away from processing, the use ease of carrying out, the difficulty of reuse, a health top problem, etc. However, a close-up of the problem accompanying the reclamation processing and incineration processing is taken, and lack of a dust reclaimed ground, the effect on the ecosystem by nondegradable plastics remaining by the environment, harmful gas generating at the time of combustion, the global warming by a lot of amounts of heat of combustion, etc. have become the cause of giving the big load to earth environment as plastics is used and discarded so much. In recent years, development of a biodegradable plastic prospers as what can solve the problem of a plastic waste. Generally a biodegradable plastic **1 Microorganism production system aliphatic series polyester called polyhydroxy alkanoate, such as Pori (3-hydroxy alkanoate), **2 Chemosynthesis system aliphatic series polyester, such as polylactic acid and the poly caprolactone, **3 It is divided roughly into three kinds [say / naturally-ocurring-polymers objects, such as starch and cellulose acetate.]. Polylactic acid and the poly caprolactone have a problem in thermal resistance also in chemosynthesis system aliphatic series polyester, and a naturally-ocurring-polymers object has the problem of being inferior to it being non-thermoplasticity or a water resisting property.
[0003]
On the other hand, polyhydroxy alkanoate is excellent in the resolvability under aerotropism and an anaerobiosis, and a toxic gas is not generated at the time of combustion, but it has the outstanding description of giant-molecule quantification being possible at the plastics originating in the microorganism which used the vegetable raw material, and being the carbon neutral which does not increase the carbon dioxide on the earth. The property decomposed especially under an anaerobiosis and the point which macromolecule quantification is possible for and exists are the engine performance which should be mentioned especially. Although this hydroxy alkanoate is classified into aliphatic series polyester, the property of a polymer differs from the aliphatic series polyester of the chemosynthesis system described previously greatly.
[0004]
Thus, since it consists of a natural component, the problem of trash is solved and polyhydroxy alkanoate is excellent in environmental compatibility, a Plastic solid applicable to wrapping, a tableware ingredient, construction, engineering works, agriculture and a horticulture ingredient,

adsorption, support, filter media, etc. is desired.
[0005]
However, there is decomposition at the time of heating as a pfoblem on processing of polyhydroxy alkanoate. Polyhydroxy alkanoate produces a pyrolysis, for example, when it heats enough to the temperature more than the melting out temperature, and when processing it at an elevated temperature 5 degrees C or more especially from a melting out temperature, molecular weight falls greatly with heating time. If molecular weight becomes low, as the evil, it will be inferior to the drawdown nature at the time of extrusion, and workability will get worse. If it fuses at the temperature more than a melting out temperature when pelletizing the polyhydroxy alkanoate of the shape of fine particles which extracted and was acquired from the microorganism inside of the body as the example, the melt strength of a melting strand is scarce and it is difficult to produce continuously that a strand tends to be turned off. Moreover, it will extrude, if melt strength is scarce also at the time of the manufacturing method of a common hollow container, and extrusion blow molding, and it is predicted that it hangs down during blow molding and is easy to fall, and it is expected that extrusion blow molding is also difficult. The resin which has high melt strength is needed for extrusion molding in sufficiently elevated temperature temperature rather than such a melting out temperature.
[0006]
In order to improve the melt strength of resin generally, it is effective to hyperviscosity-ize resin and the addition of the matter which has chemical cross-linking, addition of an inorganic substance, etc. are well known as an approach for it. As an example which applies the matter which has chemical cross-linking to aliphatic series polyester, addition (patent reference 1-3) of an isocyanate compound etc. is typical. However, although the aliphatic series polyester of a chemosynthesis system is sufficient as such an example and it is carried out, when applying to polyhydroxy alkanoate, since a meaning called the original natural product origin fades, it is considered not to be desirable. Moreover, as an example of inorganic substance addition, an inorganic bulking agent (talc) etc. is mixed with aliphatic series polyester, for example into the mixture of the poly caprolactone, melt strength is increased, and the thing of raising the workability at the time of melting shaping (patent reference 4 and 5), the method of carrying out copolymerization of the suffonic-acid metal salt into aliphatic series polyester, in order to distribute the filler which is hard to distribute, etc. are learned (patent reference 6). However, by the approach of the patent reference 4 and five publications, the about 100 to 900 section, since it is abundant, also when resin does not have compatibility, the problem was in the need for a compatibilizer, and transparency by the case, and the survival after biodegradation carries out becoming abundant and incineration processing to the resin 100 section also as for the addition of an inorganic substance, the problem that a lot of inorganic survival occurs is in a furnace. Moreover, although surely the dispersibility of the additive of a minute amount improves and various properties can be expected by the approach given in the patent reference 6, it loses that a process increases and the advantage of the original natural product origin and is not desirable if copolymerization of a certain segment is chemically carried out to polyhydroxy alkanoate.
[0007]
Moreover, there is lateness of the crystallization rate at the time of fusing at temperature sufficiently higher than a melting out temperature as another problem about the melt strength at the time of melting processing of polyhydroxy alkanoate. If a crystallization rate is slow, it will be inferior to the melt strength after melting extrusion, and drawdown nature too, and melting extrusion will become difficult. About the crystallization rate improvement, examination is made variously. As a certain melting processing method, the polyhydroxy alkanoate (PHA-X) which has a high melting out temperature, and the polyhydroxy alkanoate (PHA-Y) which has low-melt point solution temperature are mixed, and the approach of processing it at the temperature between each melting out temperatures is proposed (patent reference 7). this invention persons as a high melting out temperature component However, Pori (3-hydroxy butyrate) (melting out temperature: 176 degrees C). The result to which the hexanoate component carried out melting mixing of 11% of Pori (3-hydroxy butyrate-KO-3-hydroxy hexanoate) (melting out temperature: 115 degrees C) at 120 degrees C, and retested this processing method as a low-melt point

solution temperature component, The constituent crystallization rate obtained by this approach was not necessarily the improved object. For example, although the extrusion melt with a little early crystallization rate is obtained in case the constituent obtained by this approach is fused with an extruder and pelletizing is carried out from a melting strand, nonuniformity is in crystallization, since there is also no melt strength, a taking over rate is limited very much that it is very easy to go out, and there is a problem of not being practical. Moreover, it is proposed by obtaining the constituent to which micro-disperse of the polyhydroxy alkanoate which has higher melting out temperatures, such as Pori (3-hydroxy butyrate), was added and carried out as other examples using Pori (3-hydroxy butyrate-KO-3-hydroxy hexanoate) that a crystallization rate becomes quick (patent reference 8). It is the description that a high melting out temperature component carries out micro-disperse, and when micro-disperse of this constituent is being carried out and it obtains the temperature up curve of a constituent by DSC, it supposes that it is proved by the width of face of the endoergic peak of original Pori (3-hydroxy butyrate-KO-3-hydroxy hexanoate) being extended to an elevated-temperature side. However, the thing for which the DSC curve of Pori (3-hydroxy butyrate-KO-3-hydroxy hexanoate) is extended to an elevated-temperature side after that, It becomes clear to examination of this invention persons therefore that it may not necessarily correlate with crystallization of a constituent becoming early. In this reference It is not indicated about the approach of raising the melt strength of the melt of the Pori (3-hydroxy butyrate-KO-3-hydroxy hexanoate) constituent.
[0008]
[Patent reference 1]
JP,5-295098,A
[0009]
[Patent reference 2]
JP,7-149862,A
[0010]
[Patent reference 3]
JP,10-46013,A
[0011]
[Patent reference 4]
JP,2001-172487,A
[0012]
[Patent reference 5]
JP,11-349795,A
[0013]
[Patent reference 6]
JP,2001-323052,A
[0014]
[Patent reference 7]
Patent Publication Heisei No. 510498 [eight to] official report
[0015]
[Patent reference 8]
WO 02/50156 A2
[0016]
[Problem(s) to be Solved by the Invention]
As mentioned above, Pori (3-hydroxy alkanoate) and especially the efficient approach of being able to increase the melt viscosity of Pori (3-hydroxy butyrate-KO-3-hydroxy hexanoate) resin, raising the melt strength of melt, and a crystallization rate also raising further are not yet established. These problems are solved, and moldabilities, such as welding prevention and improvement in fine speed, are improved in the case of the shaping approach use of melting extrusion molding, melting film shaping, melt spinning, etc., and this invention is possible also for the biodegradation as a disposal means, and makes it a technical problem to offer the Pori (3-hydroxy alkanoate) constituent excellent in the environmental compatibility which disposal — there is no survival in a furnace when it destroys by fire — tends to carry out, and its

manufacture approach.
[0017]
[A means to solve invention]
Pori which has low-melt point solution temperature as a result of repeating research wholeheartedly so that this invention persons may solve the above-mentioned technical problem (3-hydroxy alkanoate) Pori which has (it is hereafter called constituent (a)) and a high melting out temperature (3-hydroxy alkanoate) When there is melt viscosity of the constituent (ab) which mixed (it is hereafter called constituent (b)) by hyperviscosity rather than the melt viscosity of the constituent (a) in a specific melting range, it finds out that the moldability at the time of melting processing improves, and a crystallization rate also improves, and came to complete this invention.
[0018]
That is, the first of this invention, it is the Pori (3-hydroxy alkanoate) constituent shown by the formula (1).
Constituent (a): The Pori (3-hydroxy alkanoate) constituent which has weight average molecular weight Mwa (1x104 <=Mwa<=3x106) and a melting out temperature Tma,
Constituent (b): The Pori (3-hydroxy alkanoate) constituent which has weight average molecular weight Mwb (1x104 <=Mwb<=1x107) and a melting out temperature Tmb (here, it is Tmb>=Tma+5 degree C),
It is the Pori (3-hydroxy alkanoate) constituent (ab) mixed and obtained,
Melt viscosity etaab in Te (however, Tma<=Te<=Tmb) of the arbitration of a constituent (ab) is related with the Pori (3-hydroxy alkanoate) constituent (ab) which has the relation of eta a<eta ab to melt viscosity etaa in Te of a constituent (a).
[0019]
[-CHR-CH2-CO-O-] ..... Formula (1)
Here, R is the alkyl group expressed with CnH2n+1, and is n=1-15.
[0020]
As the desirable embodiment, a constituent (a) to the above-mentioned constituent and pan which are Pori (3-hydroxy butyrate-KO-3-hydroxy hexanoate) A constituent (a) in Pori (3-hydroxy butyrate-KO-3-hydroxy hexanoate) The presentation ratio of the copolymerization component is Pori (3-hydroxy butyrate):Pori (3-hydroxy hexanoate) =99-80:1-20 (mol%). And the above-mentioned constituent whose constituent (b) is Pori (3-hydroxy butyrate). Or a constituent (a) and a constituent (b) are Pori (3-hydroxy butyrate-KO-3-hydroxy hexanoate). The presentation ratio of the copolymerization component of a constituent (a) by 3-hydroxy butyrate:3-hydroxy hexanoate =99-80:1-20 (mol%) And the presentation ratio of the 3-hydroxy hexanoate component of a constituent (b) is related with the above-mentioned constituent characterized by being smaller than the presentation ratio of the 3-hydroxy hexanoate component of a constituent (a). Moreover, as another desirable embodiment, the mixing ratio of the constituent (a) in a constituent (ab) and a constituent (b) is related with the above-mentioned constituent which is (a):(b) =70:30-99.9:0.1.
[0021]
How to carry out heating fusion and mix the 2nd constituent (a) of this invention, and a constituent (b), The approach of mixing in a solvent using a meltable solvent, the approach of mixing a constituent (b) in the slurry obtained in the purification phase after (Constituent a) culture, And a presentation is changed during culture of a constituent (a) and it is related with the manufacture approach of at least one or more sorts of above-mentioned constituents (ab) chosen from the group which consists of the approach of creating a constituent (b) and mixing.
[0022]
[Embodiment of the Invention]
The Pori (3-hydroxy alkanoate) constituent of this invention is a constituent which is aliphatic series polyester which consists of 3-hydroxy alkanoate shown by the formula (1), and which has structure repeatedly and which consists of Pori (3-hydroxy alkanoate).
[0023]
[-CHR-CH2-CO-O-] ..... Formula (1)

Here, R is the alkyl group expressed with CnH2n+1, and is n=1-15.
[0024]
As the Pori (3-hydroxy alkanoate) constituent (a) in this invention, and (b) The copolymer which consists of a homopolymer of the above-mentioned 3-hydroxy alkanoate, or two or more sorts of combination, These homopolymers, such as a G copolymer, the Tori-copolymer, and a tetrapod-copolymer, Two or more sorts of blend objects chosen from a copolymer etc. are mentioned. Especially The 3-hydroxy butyrate of n= 1, 3-hydroxy BARIRETO of n= 2, the 3-hydroxy hexanoate of n= 3, Homopolymers, such as 3-hydroxy octanoate of n= 5, and 3-hydroxyoctadecanoate of n= 15, Or the copolymer which consists of combination of two or more sorts of these 3-hydroxy alkanoate units, a G copolymer, the Tori-copolymers, or these blend objects can use it preferably. Although chemosynthesis of these Pori (3-hydroxy alkanoate) is carried out and they is obtained, what is produced by the microorganism from a viewpoint of the biodegradable plastic constituent of the natural product origin is desirable.
[0025]
In this invention, the relation of the melting out temperatures Tma and Tmb corresponding to each of a constituent (a) and a constituent (b) fills Tmb>=Tma+5 degree C.
[0026]
Especially, as a constituent (a), Pori (3-hydroxy butyrate-KO-3-hydroxy hexanoate) which is the copolymer of the 3-hydroxy butyrate of n= 1 and the 3-hydroxy hexanoate of n= 3 is desirable, and it is still more desirable as the presentation ratio that it is 3-hydroxy butyrate:3-hydroxy hexanoate =99-80:1-20 (mol%).
[0027]
As a constituent (b), Pori (3-hydroxy butyrate-KO-3-hydroxy hexanoate) where Pori (3-hydroxy butyrate) or the presentation ratio of a 3-hydroxy hexanoate component is smaller than the presentation ratio of the 3-hydroxy hexanoate component of a constituent (a) is desirable.
[0028]
The constituent (ab) in this invention is mixture which consists of the above-mentioned constituent (a) and a constituent (b). As for the mixing ratio of the constituent (a) in a constituent (ab), and a constituent (b), it is desirable that it is the range of 70:30 to 99.9:0.1.
[0029]
In this invention the melting out temperature of a constituent (a) and a constituent (b) A differential scanning calorimeter (it is hereafter described as DSC) is used. 1-10mg of resin with 10-degree-C programming rate for / After carrying out a temperature up to more than the assumption melting out temperature that resin fully dissolves from 30 degrees C and lowering the temperature to 30 degrees C at the temperature fall rate for 10-degree-C/subsequently, it is 10-degree-C programming rate for /again, and is the peak top temperature of the endoergic curve when carrying out a temperature up to the assumption melting out temperature of +50-60 degrees C of the resin which resin fully dissolves. The endoergic curvilinear peak when carrying out the temperature up of the constituent (a) and constituent (b) which are used for this invention again shows a single or two or more peaks. When a peak is plurality, let peak top temperature by the side of an elevated temperature be a melting out temperature. As mentioned above, 5 degrees C or more of things with which the relation of the melting out temperatures Tma and Tmb corresponding to each of a constituent (a) and a constituent (b) fills Tmb>=Tma+5 degree C, i.e., a melting out temperature difference, is a certain thing. 10 degrees C or more of this melting out temperature difference are 20 degrees C or more still more preferably preferably. The pyrolysis of polyhydroxy alkanoate becomes processible [at the temperature near the Tma side which is low-melt point solution temperature] at the time of melting processing of a constituent (ab), and can avoid the effect of the molecular weight fall at the time of processing, so that the temperature gradient of Tma and Tmb is large, since it becomes so intense that heating time turns into long duration so that whenever [stoving temperature] is an elevated temperature.
[0030]
The most important point of this invention is that melt viscosity etaab in the temperature Te (however, Tma<=Te<=Tmb) of the arbitration of the constituent (ab) which mixed the constituent

(b) and the constituent (b) has the relation of eta a<eta ab to melt viscosity etaa in Te of a constituent (a). etaa here and etaab are compared in the condition of having passed through processing and the heat history of these conditions. That is, when melting kneading of a constituent (a) and the constituent (b) is carried out in obtaining a constituent (ab), after carrying out melting kneading of the constituent (a) separately on these conditions, etaa of a constituent (a) is measured, and it compares with etaab of a constituent (ab). In this invention, giving the relational expression of eta a<eta ab shows that the melt viscosity in this temperature of a constituent (ab) is increasing to the melt viscosity at the time of carrying out melting of the constituent (a) at a certain temperature. This is the index of whether a constituent (b) does an operation to a constituent (a). The interface welding nature of that the dispersibility in the inside of the constituent (a) of a constituent (b) improves, and a constituent (a) and a constituent (b), It is thought that it changes with the crystal growth devices after heating-mixing a constituent (a) and a constituent (b) and cooling etc., and when it thickens, increase of melt strength and improvement in a crystallization rate come to be accepted.
[0031]
The weight average molecular weight of a constituent (a) and a constituent (b) is 1x104 <=Mwa<=3x106 and 1x104 <=Mwb<=1x107, respectively. When each molecular weight is smaller than 1x104, it is inferior to the melt strength of a constituent (ab), and the fine speed improvement effect at the time of extrusion etc. is not acquired. Moreover, melt viscosity is too high, and in the case of Mwa>3x106 or Mwb>1x107, carrying-out [a load may be applied to an extruder and / itself]-culture production of such resin productivity is bad, and since the resin obtained serves as an expensive rank, it is not desirable. However, even when the molecular weight of a constituent is too high, adjusting to suitable molecular weight is possible by adjusting whenever [stoving temperature], and time amount suitably, or -- for example, by setting up temperature conditions etc. suitably at the time of melting kneading, since the molecular weight decreasing rate of polyhydroxy alkanoate can be reproduced whenever [stoving temperature] when time amount and a shear rate are fixed, when the molecular weight of a constituent (a) or a constituent (b) is too high, after reducing the molecular weight to the suitable range, it can also mix and fuse, making it fall.
[0032]
The mixing ratios of the constituent (a) in the constituent (ab) in this invention and a constituent (b) are 90:10-99:1 to 80:20 to 99.5:0.5, and a pan preferably [it is / that it is desirable that it is weight % and is the range of (a):(b) =70:30-99.9:0.1, and / more desirable, and]. When there are few rates of the constituent (b) in a constituent (ab) than 0.1 % of the weight, there is an inclination which becomes inadequate [melt viscosity increase or the improvement effectiveness of a crystallization rate], and since melting working temperature is influenced of a constituent (b) and serves as an elevated temperature in [than 30 % of the weight] more, it becomes easy to pyrolyze a constituent (a) component.
[0033]
Moreover, what shows effectiveness to the constituent (a) of this invention, a constituent (b), and a constituent (ab) as a thickener or a crystalline-nucleus agent as well-known additives other than Pori (3-hydroxy alkanoate) in other biodegradability resin, such as general-purpose plastics, polylactic acid system resin, other aliphatic series polyester system resin, etc., such as aromatic polyester resin, such as polyolefin resin and polyethylene terephthalate, such as polyethylene and polypropylene, and polybutylene terephthalate, may be used together with this invention. For example, organic fiber, such as inorganic fibers, such as carbon black, a calcium carbonate, silicon oxide and a silicate, a zinc white, high site clay, a kaolin, basic magnesium carbonate, a mica, talc, quartz powder, diatomaceous earth, dolomite powder, titanium oxide, a zinc oxide, antimony oxide, a barium sulfate, a calcium sulfate, an alumina, a calcium silicate, boron nitride, crosslinked polymer polystyrene, a rosin system metal salt, and a glass fiber, a whisker, a carbon fiber, and human hair, wool, kenaf fiber, bamboo fiber, pulp fiber, be mentioned. the above-mentioned additive -- one sort -- or two or more sorts may be used.
[0034]
What is necessary is not to limit especially the mixed method of the constituent (a) of this

invention, and a constituent (b), and just to use it if needed suitably. For example, you may mix by mechanical agitation, such as a tank which has a single screw extruder, a biaxial extruder, a kneader, a gear pump, a kneading roll, and an agitator as an approach of carrying out heating fusion and mixing, and the quiescence mixer which repeats splitting and unification with the guide apparatus of flow may be applied. In the case of heating melting, it needs to be cautious of the molecular weight fall by the pyrolysis, and it is necessary to mix. Moreover, in a meltable solvent, a constituent (a) and a constituent (b) may be dissolved, you may mix, it is left in a room temperature in that case, a solvent is removed, and the resin constituent of this invention is obtained. The meltable solvent in this case is mainly a meltable solvent to a constituent (a) and a constituent (b), for example, chloroform, ethyl acetate, etc. are mentioned. Moreover, the example which may add a constituent (b) to the slurry obtained in the purification phase of a constituent (a), for example, performs methanol swabbing among the purification phases of a constituent (a) and which adds a constituent (b) in process is given. Moreover, a culture condition is changed during culture of a constituent (a), and there is also a method of creating a constituent (b) and obtaining a constituent (ab) as it is. Through a centrifugal separation process etc., after culture and purification termination separates a part for a liquid, and resin solid content, and obtains the resin constituent of this invention after reduced pressure drying.
[0035]
As an approach of carrying out heating fusion in this invention, and obtaining mixture, it is also possible to use a plasticizer together depending on the case. By using a plasticizer, it is possible to control a fall and the fall of molecular weight, and improvement in a crystallization rate can also expect the melting temperature at the time of melting mixing of the constituent (a) for obtaining a constituent (ab), and a constituent (b) depending on the case. Here, although the relation of the melt viscosity which is the requirements for this invention changes since the plasticizer was mixed, a fundamental property does not change. That is, melt viscosity etaabp of the constituent (ab) at the time of using melt viscosity etaap of the constituent (a) at the time of using the plasticizer in melting temperature Te and a plasticizer should just be eta ap<eta abp

[0036]
As a plasticizer, an ether system plasticizer, an ester system plasticizer, a phthalic-acid system plasticizer, the Lynn system plasticizer, etc. are desirable, and the ether system plasticizer from the point of excelling in compatibility with polyester, and an ester system plasticizer are more desirable. As an ether system plasticizer, polyoxy alkylene glycol, such as a polyethylene glycol, a polypropylene glycol, and a polytetramethylene glycol, etc. can be mentioned, for example. As an ester system plasticizer, the ester of aliphatic series dicarboxylic acid and fatty alcohol can be mentioned. Moreover, as aliphatic series dicarboxylic acid Oxalic acid, a succinic acid, a sebacic acid, an adipic acid, etc. can be mentioned. For example, as fatty alcohol For example, a methanol, ethanol, n-propanol, isopropanol, n-hexanol, n-octanol, 2-ethylhexanol, n dodecanol, monohydric alcohol, such as stearyl alcohol, ethylene glycol, and 1 2-propylene glycol, 1 3-propylene glycol and 1, 3-butanediol, 1 5-pentanediol, 1 6-hexandiol, Polyhydric alcohol, such as dihydric alcohol, such as a diethylene glycol, neopentyl glycol, and a polyethylene glycol, and a glycerol, trimethylol propane, and a PENTA ERIS toll, can be mentioned. Moreover, two or more sorts of blend objects chosen from these homopolymers, such as a copolymer which consists of two or more sorts of combination, the above-mentioned polyether and polyester, a G copolymer, the Tori-copolymer, and a tetrapod-copolymer, or a copolymer are mentioned. Furthermore, the esterified hydroxycarboxylic acid is considered. The above-mentioned plasticizer is not one sort or the object which may use two or more sorts and is limited to this, either.
[0037]
As other effectiveness using a plasticizer, it is possible to shift the maximum crystallization temperature of a constituent (ab) to a low temperature side more. If the maximum crystallization temperature is adjusted near a room temperature by adding a plasticizer when an elevated temperature [temperature / at the time of heating melting processing of a constituent (ab) / maximum crystallization / room temperature], there is effectiveness which can simplify other processes, such as heating crystallization care of health. Moreover, brittleness may be improved

about the mold goods by the constituent (ab), with moderate rigidity maintained.
[0038]
Moreover, as for the addition of a plasticizer, it is desirable that it is 0.1 - 50 weight section to the (Constituent a) 100 weight section. Since the plasticization effectiveness becomes is hard to be acquired, the remarkable fall of melt viscosity is seen when [than 50 weight sections] more and melt strength falls greatly when there are few additions than the 0.1 weight section, the thickening effectiveness of this invention may be offset.
[0039]
Moreover, in carrying out melting mixing of a constituent (a) and the constituent (b) using an extruder and pelletizing as a constituent (ab), in order to use a tank for a cold end and to raise a crystallization rate, it is desirable to adjust the temperature of the maximum crystallization temperature neighborhood of a constituent (ab). Cutting can use an underwater cut and well-known approaches, such as an air strand cutting method. Although especially mixed temperature is not limited, it is usually carried out at the temperature more than Tma. Although molecular weight falls by the pyrolysis when it heats to the temperature more than the melting out temperature of Pori (3-hydroxy alkanoate), conditions, such as melting temperature and the residence time, are chosen appropriately, and it is in suppressing a molecular weight fall to the minimum ***.
When molecular weight is too high, it is possible to adjust molecular weight to the suitable range with heating.
[0040]
Moreover, the secondary additive of stabilizers, such as coloring agents, such as a pigment and a color, an inorganic system or an organic system particle, an antioxidant, and an ultraviolet ray absorbent, lubricant, a release agent, water repellent, an antimicrobial agent, and others can be blended with the constituent (ab) of this invention if needed.
[0041]
The constituent (ab) of this invention can improve moldabilities, such as various fiber, yarn, a rope, textiles, knitting, a nonwoven fabric, paper, a film, a sheet, a tube, a plate, a rod, a container, a bag, components, and foam. Thus, the obtained mold goods can be used suitable for the field of agriculture, a fishing, forestry, horticulture, medicine, a health article, garments, non-garments, a package, and others.
[0042]
[Example]
Next, although the constituent (ab) and its manufacture approach of this invention are further explained to a detail based on an example, this invention is not restricted only to this example. The resin used in the example and its abbreviated name are as follows.
[0043]
PHBH: Pori (3-hydroxy butyrate-KO-3-hydroxy hexanoate)
PHB: Pori (3-hydroxy butyrate)
The evaluation approach enforced in the example is as follows.
[0044]
(1) Melting out temperature (Tm)
The SEIKO electronic industry DSC200 is used. Respectively about a constituent (a) and a constituent (b) with 1-10mg, and 10-degree-C programming rate for / A temperature up is carried out to 20 degrees C (when it is this time and PHBH, in 140 degrees C and PHB, it is 200 degrees C) of assumption melting out temperature + abbreviation which resin fully dissolves from 30 degrees C, subsequently the temperature is lowered to 30 degrees C at the temperature fall rate for 10-degree-C/, and it is 10-degree-C programming rate for /again. Resin carried out the temperature up to 50 degrees C (when it is PHBH, in 170 degrees C and PHB, it is 230 degrees C) of assumption melting out temperature + abbreviation of the fully dissolved resin, and made the endoergic curvilinear peak accompanying fusion of the resin at this time melting out temperatures Tma and Tmb. In addition, in the case of the constituent (a) and constituent (b) which are used for this example, the endoergic curvilinear peak when carrying out a temperature up again showed a single or two or more peaks, and, in two or more cases, made peak top

temperature by the side of an elevated temperature melting out temperatures Tma and Tmb about each resin.
[0045]
(2) Elongation by the side of the elevated temperature of a DSC endoergic peak
The endoergic peak at the time of a temperature up was measured by the approach same about a constituent (ab) as (1), and it investigated whether the width of face of the Tma endoergic peak originating in a constituent (a) would be extended to the elevated-temperature side.
[0046]
Y: It is extended.
N: It is not extended.
(3) Melt viscosity
About the constituent (a) and the constituent (ab), using the KYAPI log rough (made in an Oriental energy machine factory), the 1mm phix10mm dice was used, based on Tma measured above (1), melting was carried out at the temperature Te more than Tma, and melting extrusion and each melt viscosity etaa and etaab were measured for the constituent in shear rate 122sec-1.
[0047]
Viscosity judging
O :eta a<eta ab
x: eta a)=eta ab
(4) Melt strength
About the constituent (ab), the extrusion strand obtained at the time of measurement of the above (2) was taken over with the take off unit installed in the location whose location from a dice outlet is 60cm. At that time, the appearance linear velocity in dice opening is 0.9 m/min, and evaluated melt strength by the taking over rate.
[0048]
O : it is possible for a strand not to be turned off but to take over by 2.0 m/min.
O : it is possible for a strand not to be turned off but to take over by 1.0 m/min.
x: A strand is turned off by 1.0 m/min.
(5) Crystallization time amount
Time amount after it comes out of a dice the extrusion strand obtained at the time of measurement of the above (2) and through and surface adhesiveness come a 60-degree C water bath out of a dice immediately about a constituent (ab) until it loses was made into crystal solidification time amount, and crystal solidification nature was evaluated.
[0049]
O : solidification time amount is 10 or less secs.
O : solidification time amount is 10-60sec.
x: Solidification time amount is 60 or more secs.
(6) Extrusion-molding nature
About the constituent (ab), the lab omnipotent extruder (phi35 kneader RUDA (KR-35): made in a Kasamatsu, Inc. chemically-modified lab) was used, dice 3 phi3mm hole was attached, melting and a strand were created at predetermined temperature, and the tank of 3m length which carried out temperature control to 60 degrees C was pelletized through through and a pelletizer.
[0050]
O : a strand is not turned off and does not have adhesion of pellets, either.
x: A strand is turned off, or pellets cannot stick and process it.
(Example 1)
Constituent (a) :P As opposed to the HBH resin (3HH=88.3 [3HB/]/11.7 (mol%), Mwa = 1,120,000 Tma=115 degree C) 100 weight section (Constituent b)-HB powder (the Mitsubishi Gas Chemical make, BIOGURIN, and Mwb= — 600,000 —) After carrying out the dryblend of the Tmb=175-degree-C3 weight section, using the lab PURASUTO mill (made in an Oriental energy machine factory), melting kneading was carried out for 3 minutes under 15rpm and conditions with a heater temperature of 160 degrees C, and the rice cake-like constituent was obtained. After cutting out and chip-izing the obtained constituent (ab1) and measuring the melting out

temperature, the melt viscosity in Te, melt strength, and crystallization time amount were measured in the KYAPI log rough. A result is shown in Table 1. Constituent (b) As compared with the constituent (a1) kneaded with the PURASUTO mill, it was etaa1<etaab1 between this temperature, this rotational frequency, and coincidence nothing. Moreover, although Tma was not extended to an elevated-temperature side in DSC measurement of a constituent (ab1), the constituent (ab1) excellent in melt strength and crystallization time amount was able to be obtained.
[0051]
[Table 1]

実施例1					参考
組成物			ab1	判定	a1
Mw(万)			92		92
Tma由来溶融ピーク(℃)			115		
Tmb由来溶融ピーク(℃)			175		
吸熱ピークの伸び			N		
溶融粘度	Te	140℃	33752	○	32065
η(poise)		150℃	29252	○	28127
結晶化時間	Te	140℃	30	○	
sec		150℃	60	○	
溶融強度	Te	140℃		○	
		150℃		○	

(Example 2)
Constituent (a) :P As opposed to the HBH resin (3HH=88.3 [3HB/]/11.7 (mol%), Mwa = 1,120,000 Tma=115 degree C) 100 weight section (Constituent b)-HB powder (the Mitsubishi Gas Chemical make, BIOGURIN, and Mwb= — 600,000 —) After carrying out the dryblend of the Tmb=175-degree-C3 weight section, using the lab PURASUTO mill (made in an Oriental energy machine factory), melting kneading was carried out for 3 minutes under 15rpm and conditions with a heater temperature of 190 degrees C, and the rice cake-like constituent was obtained. After cutting out and chip-izing the obtained constituent (ab2) and measuring the melting out temperature, the melt viscosity in Te, melt strength, and crystallization time amount were measured in the KYAPI log rough. A result is shown in Table 2. Constituent (b) As compared with the constituent (a2) kneaded with the PURASUTO mill, it was etaa2<etaab2 between this temperature, this rotational frequency, and coincidence nothing. Moreover, in DSC measurement of a constituent (ab2), Tma is extended to the elevated-temperature side and was able to obtain the constituent (ab2) excellent in melt strength and crystallization time amount.
[0052]
[Table 2]

実施例2					参考
組成物			ab2	判定	a2
Mw(万)			49		49
Tma由来溶融ピーク(℃)			115		
Tmb由来溶融ピーク(℃)			165		
吸熱ピークの伸び			Y		-
溶融粘度	Te	140℃	37128	○	23908
η(poise)		150℃	28127	○	20251
		160℃	20251	○	19408
結晶化時間	Te	140℃	3	◎	
sec		150℃	5	◎	
		160℃	15	○	
溶融強度	Te	140℃		○	
		150℃		○	
		160℃		○	

(Example 3)
Constituent (a) :P As opposed to the HBH resin (3HH=88.3 [3HB/]/11.7 (mol%), Mwa = 1,120,000 Tma=115 degree C) 100 weight section (Constituent b)-HB powder (the Mitsubishi Gas Chemical make, BIOGURIN, and Mwb= — 600,000 —) After carrying out the dryblend of the Tmb=175-degree-C0.5 weight section, using the lab PURASUTO mill (made in an Oriental energy machine factory), melting kneading was carried out for 3 minutes under 15rpm and conditions with a heater temperature of 190 degrees C, and the rice cake-like constituent was obtained. After cutting out and chip-izing the obtained constituent (ab3) and measuring the melting out temperature, the melt viscosity in Te, melt strength, and crystallization time amount were measured in the KYAPI log rough. A result is shown in Table 3. Constituent (b) As compared with the constituent (a3) kneaded with the PURASUTO mill, it was etaa3<etaab3 between this temperature, this rotational frequency, and coincidence nothing. Moreover, although Tma was not extended to an elevated-temperature side in DSC measurement of a constituent (ab3), the constituent (ab3) excellent in melt strength and crystallization time amount was able to be obtained.
[0053]
[Table 3]

実施例3					参考
組成物			ab3	判定	a3
Mw(万)			49		49
Tma由来溶融ピーク(℃)			115		
Tmb由来溶融ピーク(℃)			未検出		
吸熱ピークの伸び			N		-
溶融粘度	Te	140℃	25877	○	23908
η(poise)		150℃	21939	○	20251
		160℃	20814	○	19408
結晶化時間	Te	140℃	3	◎	
sec		150℃	5	◎	
		160℃	30	○	
溶融強度	Te	140℃		○	
		150℃		○	
		160℃		○	

(Example 4)

Constituent (a) :P As opposed to the HBH resin (3HH=88.3 [3HB/]/11.7 (mol%), Mwa = 1,120,000 Tma=115 degree C) 100 weight section (Constituent b)-HB powder (the Mitsubishi Gas Chemical make, BIOGURIN, and Mwb= — 600,000 —) After carrying out the dryblend of the Tmb=175-degree-C3 weight section, using the lab PURASUTO mill (made in an Oriental energy machine factory), melting kneading was carried out for 30 minutes under 15rpm and conditions with a heater temperature of 190 degrees C, and the rice cake-like constituent was obtained. After cutting out and chip-izing the obtained constituent (ab4) and measuring the melting out temperature, the melt viscosity in Te, melt strength, and crystallization time amount were measured in the KYAPI log rough. A result is shown in Table 4. Constituent (b) As compared with the constituent (a4) kneaded with the PURASUTO mill, it was etaa4<etaab4 between this temperature, this rotational frequency, and coincidence nothing. Moreover, in DSC measurement of a constituent (ab4), Tma is extended to the elevated-temperature side and was able to obtain the constituent (ab4) excellent in melt strength and crystallization time amount.
[0054]
[Table 4]

実施例4					参考
組成物			ab4	判定	a4
Mw(万)			12		12
Tma由来溶融ピーク(℃)			115		115
Tmb由来溶融ピーク(℃)			165		
吸熱ピークの伸び			Y		-
溶融粘度	Te	120℃	21658	○	7313
η(poise)		130℃	13220	○	6019
結晶化時間	Te	120℃	3	◎	
sec		130℃	5	◎	
溶融強度	Te	120℃		○	
		130℃		○	

(Example 1 of a comparison)
Constituent (a) :P As opposed to the HBH resin (3HH=88.3 [3HB/]/11.7 (mol%), Mwa = 1,120,000 Tma=115 degree C) 100 weight section (Constituent b)-HB powder (the Mitsubishi Gas Chemical make, BIOGURIN, and Mwb= — 600,000 —) After carrying out the dryblend of the Tmb=175-degree-C3 weight section, using the lab PURASUTO mill (made in an Oriental energy machine factory), melting kneading was carried out for 3 minutes under 15rpm and conditions with a heater temperature of 120 degrees C, and the rice cake-like constituent was obtained. After cutting out and chip-izing the obtained constituent (ab5) and measuring the melting out temperature, the melt viscosity in Te, melt strength, and crystallization time amount were measured in the KYAPI log rough. A result is shown in Table 5. Constituent (b) As compared with the constituent (a5) kneaded with the PURASUTO mill, it was etaa5 >=etaab5 between this temperature, this rotational frequency, and coincidence nothing. Moreover, in DSC measurement of a constituent (ab5), Tma was not extended to an elevated-temperature side, but became the constituent (ab5) which was inferior to melt strength and crystallization time amount as compared with the example.
[0055]
[Table 5]

比較例1					参考
組成物			ab5	判定	a5
Mw(万)			108		108
Tma由来溶融ピーク(℃)			115		115
Tmb由来溶融ピーク(℃)			175		
吸熱ピークの伸び			N		-
溶融粘度η(poise	Te	130℃	32627	×	33752
結晶化時間(sec)	Te	130℃	80	×	
溶融強度	Te	130℃		×	

(Example 2 of a comparison)
Constituent (a) :P As opposed to the HBH resin (3HH=88.3 [3HB/]/11.7 (mol%), Mwa = 1,120,000 Tma=115 degree C) 100 weight section (Constituent b)-HB powder (the Mitsubishi Gas Chemical make, BIOGURIN, and Mwb= — 600,000 —) After carrying out the dryblend of the Tmb=175-degree-C3 weight section, using the lab PURASUTO mill (made in an Oriental energy machine factory), melting kneading was carried out for 30 minutes under 15rpm and conditions with a heater temperature of 120 degrees C, and the rice cake-like constituent was obtained. After cutting out and chip-izing the obtained constituent (ab6) and measuring the melting out temperature, the melt viscosity in Te, melt strength, and crystallization time amount were measured in the KYAPI log rough. A result is shown in Table 6. Constituent (b) As compared with the constituent (a6) kneaded with the PURASUTO mill, it was etaa5 >=etaab6 between this temperature, this rotational frequency, and coincidence nothing. Moreover, in DSC measurement of a constituent (ab6), Tma was not extended to an elevated-temperature side, but became the constituent (ab6) which was inferior to melt strength and crystallization time amount as compared with the example.
[0056]
[Table 6]

比較例2					参考
組成物			ab6	判定	a6
Mw(万)			96		96
Tma由来溶融ピーク(℃)			115		115
Tmb由来溶融ピーク(℃)			175		
吸熱ピークの伸び			N		-
溶融粘度η(poise	Te	130℃	29815	×	30502
結晶化時間(sec)	Te	130℃	70	×	
溶融強度	Te	130℃		×	

[0057]
[Effect of the Invention]
According to this invention, the melt viscosity of Pori (3-hydroxy alkanoate) (constituent (a)) by making it increase by adding Pori (3-hydroxy alkanoate) (constituent (b)) of a high melting out temperature By raising the melt strength of melt and raising a crystallization rate, melting extrusion molding, Moldabilities, such as welding prevention and improvement in line speed, are improved in the case of the shaping approach use of melting film shaping, melt spinning, etc., and the biodegradation as a disposal means is also possible. When it destroys by fire, the polyhydroxy alkanoate constituent excellent in the environmental compatibility which disposal — there is no survival in a furnace — tends to carry out is obtained.

[Translation done.]